Hydrogen bonding investigation of poly(3-hydroxybutyrate) / glycol chitosan blends studied by infrared and terahertz spectroscopies

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Abstract. Poly(3-hydroxybutyrate) (PHB)/glycol chitosan (GC) polymer blend was developed as one of the new biopolymer materials. Effects of different PHB / GC concentrations were analysed as a function of the blend compositions by using Fourier transform infrared (FTIR) and terahertz (THz) spectroscopies to investigate the changes in the higher-order structure and bonding of hydrogen. The higher-order structure and hydrogen bonding monitored in this study include the crystalline structure and (C=O···H-C) hydrogen bonding of PHB. The FTIR and THz spectra showed that PHB's higher-order structure transforms into the less-order structure by adding GC without altering the crystalline structure and PHB's intramolecular (C = O ... H-C) hydrogen bonding with increasing GC concentration. Because of the addition of GC, the intensity ratio of THz bands figure out the crystalline dynamics of PHB, the helical structure deformation occurs first followed by the weakening of intramolecular (C = O ... H-C) hydrogen bonding within PHB-PHB molecules.

Keywords: Chitosan, higher-order structure, hydrogen bonding, low-frequency vibrational spectroscopy

1. Introduction

Polymers are now available in tremendous quantity and variety of materials to accommodate the needs of modern society. They can be produced in numerous applications such as energy, information technology, medical, living, and environment. However, most of them are made from traditional petroleum derivatives that cannot be decomposed in natural environment leading to major earth-environmental pollution problem [1,2]. The excessive usage of these fuel-based polymeric materials will also result in the depletion of unrenewable petroleum resources [3]. As a result, development of new biopolymers, polymers of biological origin are expected as a material to replace petroleum-based polymers. Biopolymer is characterized by biocompatibility, biodegradability, and adsorptive ability that is suitable for the application in contact with living organisms [4].

Bacteria synthesized poly(3-hydroxybutyrate) or PHB is the most known biopolymer from polyhydroxyalkanoates (PHAs) family; it is a linier polyester of biological origin (Fig. 1a). Its biodegradability and biocompatibility make PHB in high demand for wide-range of utilizations. However, the potential applications of PHB are limited by its physical properties; PHB shows high

crystalline feature and narrow processing thermal condition [5,6]. Therefore, the modification of PHB is needed to improve those properties. Here, we have modified PHB by blending technique with glycol chitosan or GC (Fig. 1b). It is a polysaccharide chitosan derivative which enhanced water solubility. GC also has biodegradable and biocompatible properties; thus PHB/GC will result as a fully biodegradable PHB-based polymer system [7].

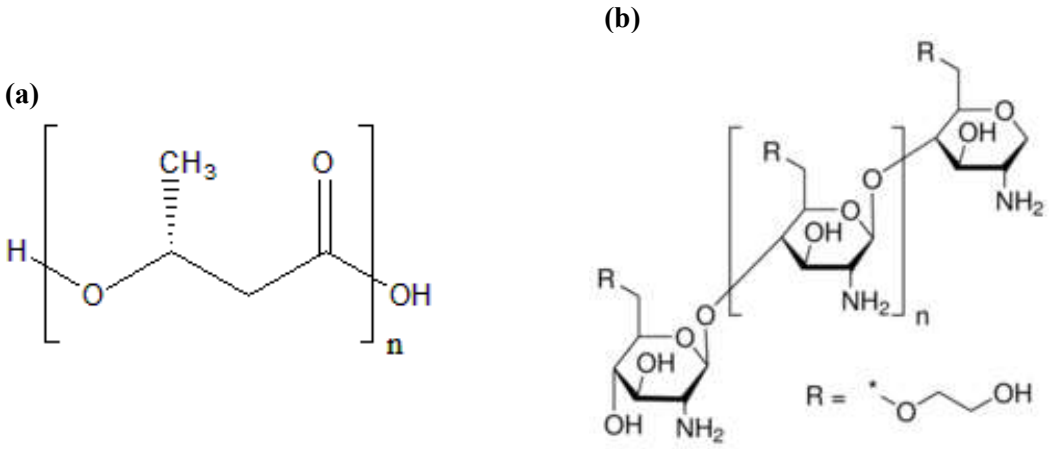

Figure 1. (a) Chemical structure of poly(3-hydroxybutyrate) (PHB) and (b) glycol chitosan (GC).

Hydrogen bonding is expected to play an important role in stabilizing the higher-order structure of polymers. Previous differential scanning calorimetry (DSC), X-ray, infrared, and Raman studies have reported the existence of weak (C=O···H-C) hydrogen bonding interaction (around 5 kJmol^{-1}) between C=O and CH_3 groups in the crystalline structure of PHB [5,6,8,9]. Information related to this hydrogen bonding can also be observed directly in the low-frequency region (3.3–330 cm^{-1}) using terahertz (THz) spectroscopy. Since low-frequency vibrational spectra are derived from intra and intermolecular interactions, THz spectroscopy can be powerful tool to reveal the formation of higher-order structures of not only homopolymer but also modified polymer. The investigation of homopolymer PHB, PHB-based copolymer and PHB-based polymer blend systems; poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(HB-*co*-HV)) and PHB/poly(4-vinylphenol) (PVPh) by using low-frequency vibrational spectroscopy have been successfully performed in the previous study [10-14]. By investigate temperature, polarized dependence together with quantum chemical calculation, the bands appeared in the region 120–70 cm^{-1} of THz spectra was assigned to vibrational motion of (C=O···H-C) hydrogen bonding of PHB [10-12]. The study of (P(HB-*co*-HV)) successfully reported the crystalline structure change from PHB-type structure to PHV-type, as shown in the infrared and X-ray studies [13,15]. PHB/PVPh study progressively reported the formation of new peak due to intermolecular hydrogen bonding between PHB and PVPh molecules [14]. In this study we attempted to elucidate the change in the higher-order structure and hydrogen bonding formed by polymer blends of PHB and glycol chitosan.

2. Methods

2.1. Materials and sample preparation

Low-molecular weight PHB (MW ~1000) was supplied from Polysciences, Inc. and glycol chitosan (purity ≥ 60%, degree of deacetylation = 91.6%) [16] was purchased from Sigma-Aldrich Co., they were used as received without any purification process. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was supplied by Wako Pure Chemical Industries, Ltd. Samples of PHB/GC blends were prepared by dissolving PHB and glycol chitosan in HFIP with prescribed weight percentage. The films were prepared by pouring the solution of blend samples on an aluminium dish, followed by evaporation at 20℃, and then continued by drying in a vacuum oven at 70℃ for 12h.

2.2. Measurements

A Thermo Nicolet Nexus 470 FTIR equipped with a liquid nitrogen cooled system and a mercury cadmium telluride (MCT) detector was used to perform Fourier transform infrared (FTIR) spectra of the PHB / GC blend films. The measurements were performed using Microm ATR with 128 scans at a 2 cm^{-1} resolutions. On the other hand, THz spectra of the blend films were measured by using a terahertz time-domain spectrometer (THz-TDS), TAS7400TS from ADVANTEST Co. The spectra were obtained in the transmission mode in the 120–60 cm^{-1}region with 1024 scans and 0.25 cm^{-1} spectral resolution.

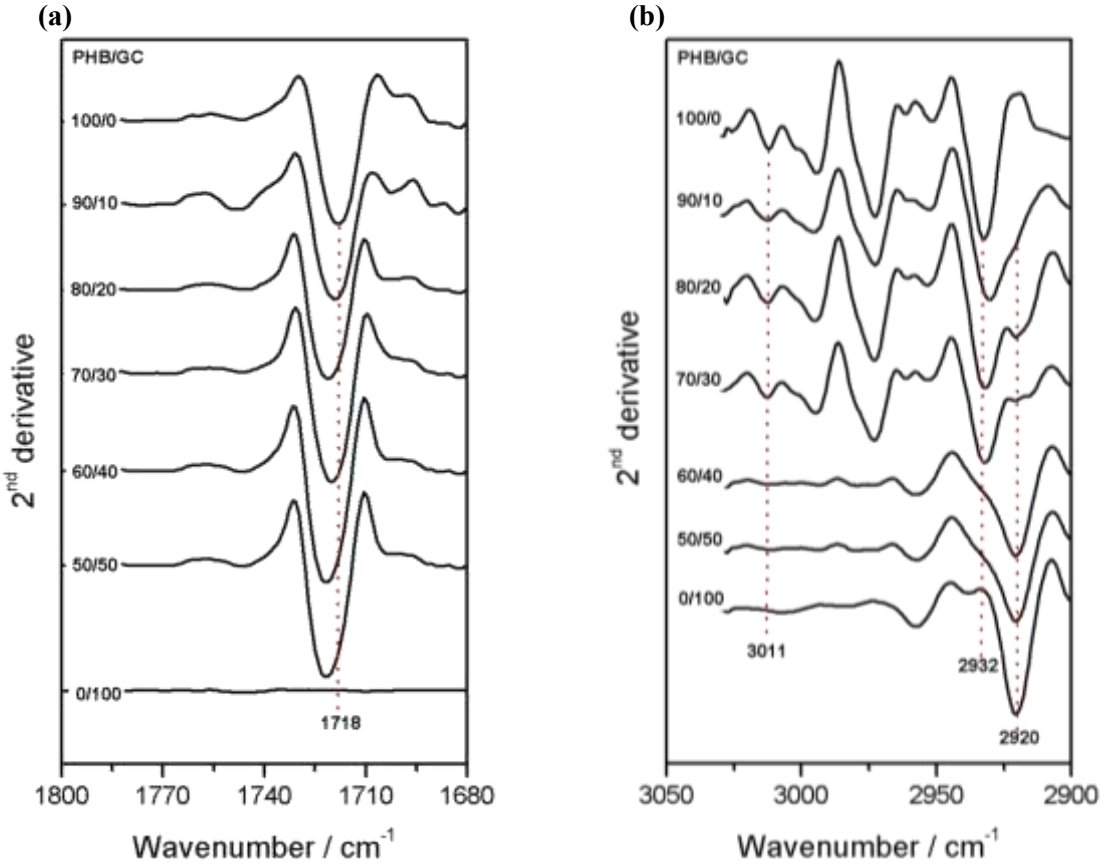

Figure 2. Second derivative FTIR spectra of PHB/GC with various blending ratios in the (a) C=O stretching and (b) C-H stretching region.

3. Results and discussion

3.1. Composition-dependent spectra in the C=O stretching and C-H stretching region

Figure 2 shows the second derivative FTIR spectra obtained at room temperature for the film samples of pure PHB, PHB/GC blends with increasing GC concentrations, and pure GC; (100/0), (90/10), (80/20), (70/0), (60/40), (50/50), and (0/100) in the C=O stretching and C-H stretching region. In the region of 1800–1680 cm^{-1}, PHB shows a sharp band centred at 1718 cm^{-1} due to C=O stretching mode of PHB in the crystalline state [5]. This band refer to intramolecular (C=O···H-C) hydrogen bonding interaction between C=O group in one helix and the CH_3 group in another helix of PHB molecules [6]. On the other hand, pure GC does not any show any band since there is no carbonyl group in its chemical structure (Fig. 1(b)).

In Fig. 2a, position of the band related to the intramolecular C=O gradually shifts to the higher wavenumber from 1718 to 1724 cm^{-1} with increasing the GC concentrations in the blends. It indicates

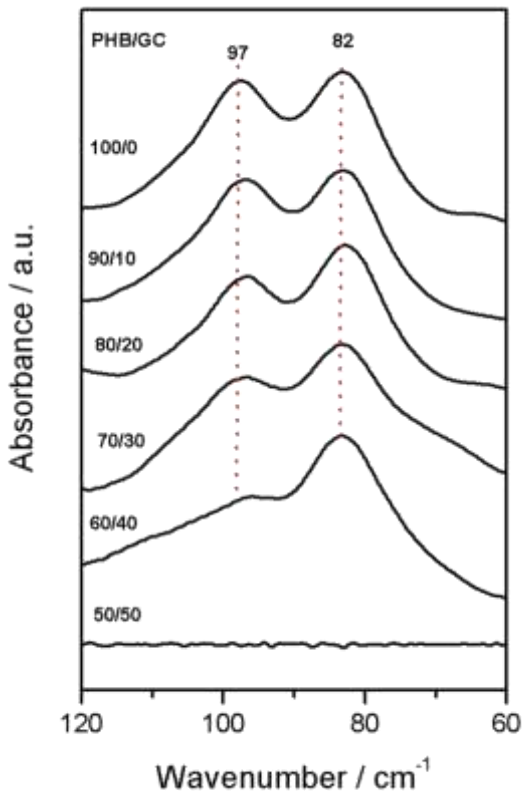

Figure 3. THz spectra of PHB/GC with various blending ratios.

that the intramolecular (C=O ⋯ H-C) hydrogen bonding of PHB weaken by the addition of GC. A band appears at 3011cm^{-1} in the C-H stretching region (Fig. 2b) has been assigned to the C-H stretching mode of the (C=O ⋯ H-C) hydrogen bonding of the PHB higher-order structure [5]. The band at 3011 cm^{-1} gradually decreases with increasing GC concentration in the blends from PHB/GC (100/0), (90/10), (80/20), (70/0) and completely disappears when PHB ≤ 60%, indicating that the higher-order structure of PHB is destructed by the addition of GC. Therefore, when the concentration of GC increases, the development of higher-order structure of PHB becomes difficult in these blend samples. This band's location does not change with that concentration of GC relative to pure PHB, it explains the PHB's crystalline structure does not change through mixing with GC.

3.2. Composition-dependent THz spectra of PHB/GC

Figure 3 shows the THz spectra of pure PHB and PHB/GC blends with increasing the GC concentrations in the region of 120–60 cm^{-1} collected at room temperature. They are two bands centred at 97 and 82 cm^{-1}. The band at 97 cm^{-1} was assigned to the out-of-plane CH_2 and CH_3 vibrations which directed to spring like motion of helical structure. On the other hand, the band at 82 cm^{-1} was assigned to the out of plane C=O and CH_3 vibrations which directly reflect the intramolecular (C=O···H-C) hydrogen bonding of PHB crystalline state [12].

The absorbance of the bands at 97 and 82 cm^{-1} gradually decreases with increasing GC concentration in the blends from PHB/GC (100/0), (90/10), (80/20), (70/30) to (60/40) and completely disappear in the PHB/GC (50/50). Plots of the absorbance of these bands versus PHB concentrations can be seen in Fig. 4a. In detail, the reduction of the band at 97 cm^{-1} reveals the transformation of PHB helical structure from the higher-order to less-order structure. While the reduction of the band at 82 cm^{-1} indicates that the intramolecular (C=O···H-C) hydrogen bonding within PHB weaken with increasing GC concentration. However, the position of these bands does not show any significant change with variation in the blend concentration means there is no change in the crystalline structure of PHB. It is consistent with the higher-frequency vibrational region results. The crystalline dynamics of PHB/GC can also be figured out by exploring the change of PHB intensity ratio due to the blends. In the Fig. 4b, it is clear that the intensity ratio of the two bands at 97 and 82 cm^{-1} gradually decreases with reduction of the PHB concentration. It indicates that the deformation of helical structure happens first followed by the weakening of intramolecular (C=O···H-C) hydrogen bonding within PHB-PHB molecules.

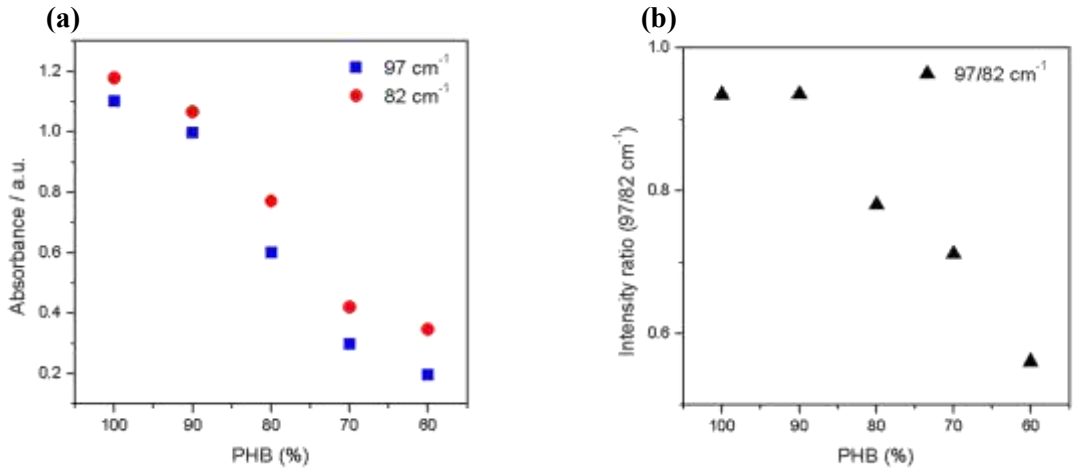

Figure 4. (a) Plots of absorbance and (b) intensity ratio of the bands at 97 and 82cm^{-1} relative to PHB concentrations.

4. Conclusion

The change in the higher-order structure and hydrogen bonding formed by polymer blends of PHB and glycol chitosan with various blending concentration has been investigated by FTIR and THz spectroscopies. Through introducing glycol chitosan to the PHB, FTIR spectra revealed the band's lower wavenumber changes at 1718 cm^{-1} as a result on the weakening of intramolecular (C=O···H-C) hydrogen bonding between PHB-PHB molecules. In contrast, the 3011 cm^{-1} band reduces and disappears completely once PHB ≤ 60%, suggesting that PHB's higher-order structure is disrupted by the introduction of GC. THz spectra showed band reduction at 97 and 82 cm^{-1} suggests that higher-order PHB structure transforms into lower-order structure and intramolecular (C=O···H-C) hydrogen bonding within PHB weakened with increasing concentration of GC, respectively. The frequency ratio of THz bands revealed that helical structure deformation occurs first, followed by the weakening of intramolecular (C=O···H-C) hydrogen bonding between PHB-PHB molecules.

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